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(19) (CA) **CANADIAN PATENT** (12)

(54) Brass Alloy, Manufacturing Process and Use

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Abstract of the Disclosure

The invention relates to a brass alloy, and its method of preparation having the following composition (in % by weight): 10 to 35% zinc 4 to 12% manganese, 2 to 7% aluminium, 1.1 to 4% silicon, 0.01 to 0.15% chromium and/or zircon, provided that the silicon is bound for the most part in the form of manganese silicide, and optionally up to 2% lead, up to 2% nickel, up to 1% usual impurities, whereby the portion of iron impurities may not exceed 0.7%, the remainder being copper. The brass alloy material is particularly useful for making synchronizing disks because of its high resistance to wear and good workability.

The present invention relates to a brass alloy, a method for its manufacture or a semi-finished product from such a brass alloy, as well as use of the brass material or brass alloy for semi-finished goods and intermediate products which must exhibit, in addition to good workability, a high resistance to wear, particularly for synchronizing disks.

Various materials, such as high-strength brass and aluminium alloys, but also composite materials such as high-strength brass coated with hard metals and the like are used for synchronizing disks. The latter are thereby restricted in their application for reasons of cost to only special uses, whereas problems with respect to wearing quality increase with high-strength brasses or aluminium alloys as a result of constantly rising requirements particularly in the manufacture of automobiles.

The present invention is directed to providing a brass alloy or brass material which meets the increasing requirements with respect to wearing quality.

Thus according to the present invention, there is provided a brass alloy of the following composition (in % by weight) is proposed in accordance with the invention:

10 to 35% zinc

4 to 12% manganese

2 to 7% aluminium

1.1 to 4% silicon

0.01 to 0.15% chromium and/or zircon

provided that the silicon is bound for the most part in the form of manganese silicide, as well as optionally



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up to 2% lead

up to 2% nickel

up to 1% usual impurities,

whereby the portion of iron impurities may not exceed 0.7%,

remainder copper.

Such an alloy has in particular the advantage that it can be manufactured from relatively inexpensive components and yet attain desired technical properties. In particular, alloying constituents which generally can only be melted in the form of particularly expensive master alloys, such as iron for example, are not necessary or are only present in small amounts as an impurity.

Alloys based on Cu-Zn-Al of the above-noted composition are to be allocated, from a technical aspect with regard to alloys, to high-strength brasses. Such alloys are widely used for wear-resistant parts, for example synchronizing disks.

Thus, it is known from applicant's German O.S. 29 19 478 to use a brass alloy for synchronizing disks having the following composition:

60 to 75% copper

6 to 8% manganese

4 to 6% aluminium

1 to 4% silicon

1 to 3% iron

0.5 to 1.5% lead

optionally up to 0.2% nickel

up to 0.2% tin

up to 0.05% of one or several of the elements chromium,

vanadium, titanium

remainder zinc

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The relatively high wear resistance achieved in this case is attributed to the intermetallic compounds formed from iron, manganese and silicon. The additions of chromium, vanadium and titanium, in addition to iron, appear to contribute to grain refining of the structure. Higher costs arise with this alloy, particularly on account of the relatively high iron content of 1.6% by weight since it can, on the one hand, only be introduced by means of an expensive master alloy and, on the other hand, is essential for the formation of a particularly fine-grained structure.

10 Furthermore, a brass alloy resistant to wear at high temperatures and which can be used as valve seat material for internal combustion engines can be gleaned from the German patent 21 45 690. Such parts must have features similar to synchronizing disks, particularly a uniform co-efficient of friction. When used for valve seats, the co-efficient of friction must be as low as possible, whereas the co-efficient of friction for synchronizing disks should be as high as possible. Such a brass alloy has the following composition:

25	to 40%	zinc
1	to 8%	aluminium
1	to 5%	manganese
0.8	to 3%	chromium
0.3	to 2%	silicon
0.3	to 1%	phosphorous

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optionally up to 2% iron and/or nickel and further optional components, whereby the optional components may not exceed 5% all told remainder copper

Aluminium and chromium are to strengthen the crystal matrix and contribute to improving the wear resistance; silicon forms, together with manganese, a hard intermetallic compound which likewise contributes to increasing wear resistance. Phosphorous serves as a deoxidizer and should likewise

increase the hardness of the material.

Through deposit of aluminium in the copper-zinc matrix (by "bracing" the original lattice), there is a mixed crystal hardening in such Cu-Zn-Al base alloys. These alloys acquire wear resistance through intermetallic compounds (silicides), in particular of the metals iron and manganese with silicon. The wear resistance thereby increases within a specific range with the amount of silicide. It is generally endeavoured to increase the amount of silicides and thus the wear resistance.

10 However, with the increasing amount of silicides, the risk also increases that very coarse silicide precipitations will form, and that the silicides will coagulate into clumps masses or solid complexes. Both processes increase the risk of brittle fracture in parts made from such alloys. However, brittle fracture in such parts as synchronizing disks, for example, is extremely undesirable since considerable consequential damage can arise as a result.

In addition, such silicide concentrations automatically occur opposite regions poor in silicides which in every case results in inadequate wear resistance in the affected parts.

20 The silicon content in the relevant wrought alloys is thus limited according to DIN (German Industrial Standard) 17 660, CuZn40Al 1 and 2 to contents up to a maximum of 1% by weight. Silicon contents up to 2% by weight maximum in such alloys are an exception. Higher silicon contents in such alloys are thus hardly realizable.

However, a silicon content of up to 4% by weight appears to be claimed in the German O.S. 29 19 478, although, the preferred exemplary embodiment cites a silicon content of only 1.5% by weight. In actual fact, the alloy can only preferably be used, in accordance with the indicated purpose, with a silicon content of approximately 1.7% by weight maximum.

German patent 21 45 690 also claims up to 2% silicon, whereas its

exemplary embodiments exhibit a silicon content of maximum 0.8%.

Maximum silicon contents of 1.53% for such alloys were tested by an alloy manufacturer (Automobiltechnische Zeitschrift [periodical of automotive engineering] 83 (1981) 227 - 230).

Thus, it is generally relatively difficult to accommodate larger quantities of silicide in a practical manner in Cu-Zn-Al material. Moreover, it is also not possible to use any desired methods which appear suitable for refinement and blending of the silicide precipitations. Surprisingly, it was established that a reduction of silicides with the same volume portion results in a clear deterioration of the wear resistance.

It is thus necessary to ensure for a silicide quantity adequate for the required increased wear resistance that, in addition to a homogeneous distribution, the silicides are also a specific average size within a predetermined size range.

This is possible in accordance with the present invention by means of specific contents of chromium and/or zircon in the brass alloy. The chromium contents range between 0.01 and 0.15% by weight, preferably between 0.05 and 0.1% by weight, as a function, on the one hand, of the silicon content and, on the other hand, also to a small extent on the remaining alloy constituents.

Normally, lower contents of chromium and/or zircon have no effect on the silicide precipitation and higher contents result in unfavourably fine silicide precipitations which considerably reduce the wear-resistance. Chromium and zircon can thereby respectively be replaced and can also be used additively. The amount of chromium and/or zircon to be added must respectively be ascertained as a function of all constituents of the alloy. It was thus surprisingly established, for example, that with higher aluminium contents, the addition of chromium or zircon must also be increased in order to obtain the same form of

silicide precipitations. With too high an addition of chromium or zircon, coarse agglomerations of the precipitations occur in addition to the fine silicide precipitations, whereby such a brass alloy to a large extent also becomes useless.

For the brass alloy according to the invention a surprisingly selective method results for controlling the form and distribution of the silicide precipitations with respect to the wear resistance and breaking strength of a corresponding material.

Further advantages and advantageous embodiments of the invention will become apparent from the following description. The structure of the material according to the invention is considered in detail using the accompanying drawings, in which:

Figures 1 and 2 are micrographs of a Cu-Zn-Al material with and without a chromium content,

Figures 3 and 4 are micrographs of a Cu-Zn-Al material with and without a chromium content,

Figures 5 to 7 are micrographs of essentially identical Cu-Zn-Al materials with differing chromium contents.

The following meanings apply for the terms alloy, material and semi-finished good or intermediate product used in the following:

alloy - relates quite generally to the chemical composition;

material - "finished alloy" includes chemical composition and structure;

semi-finished good or intermediate product - relates to material which already has a specific external shape and which still requires further processing up to the end product.

The alloy according to the invention is composed of the following constituents (all particulars for the composition in the following are in % by

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weight):

10 to 35% zinc
4 to 12% manganese
2 to 7% aluminium
1.1 to 4% silicon
0.01 to 0.15% chromium and/or zircon
optionally up to 2% lead
up to 2% nickel
up to 1% usual impurities
remainder copper

The manganese content is coupled to the respective silicon content in that it is predetermined that the silicon is bound for the most part in the form of manganese silicide.

For the impurities, it is furthermore predetermined that the total portion of iron impurities may not exceed 0.7%.

In a material having this alloy composition, copper, zinc and aluminium form the basic structure. The respective range of limits for these constituents is predetermined for the most part by the usual requirements relating to hardness and workability of the material. A β -structure or a $\beta+\alpha$ - structure should arise for this material. δ -structure portions are to be avoided if possible.

The lower and upper limits for the manganese and silicon portions are related to one another, i.e. 1.1% silicon or 4% silicon require for the alloy composition according to the invention approximately 4% manganese or 12% manganese respectively in order that it can be completely bound as silicides. Furthermore, the lower limits result from a minimum amount of silicides of

approximately 5% necessary for wear resistance. The upper limits of 12% manganese or 4% silicon result from the maximum silicide amount of approximately 16% that can appropriately be introduced into the basic structure. Moreover, uneven silicide precipitations result which negatively influence the wear resistance. Preferably, silicon contents between 2 and 3% are used in conjunction with manganese contents above 6% since the most balanced material properties result in this range for the preferred use of the alloy for synchronizing disks.

Chromium and/or zircon are added in the range totalling between 0.01% and 0.15% and influence the silicide precipitation. Below approximately 0.01 chromium or zircon content no more substantial influences on the silicide precipitation occur, while with portions above approximately 0.15% the silicide precipitations are too fine and as well can form coarse agglomerations. Chromium or zircon can be used optionally or also additively. The respective amount of chromium and/or zircon to be added depends on the silicon quantity and the desired form of the silicide precipitations as well as to a lesser degree on the portions of the remaining constituents, particularly the aluminium content, namely such that with an increasing silicon quantity, refinement of the silicide precipitations and increasing aluminium portion a higher chromium content is necessary. The chromium contents preferably lie between 0.05 and 0.1% since this results in the most balanced material properties for the preferred use for synchronizing disks.

According to previous knowledge, the mechanism for influencing the silicide precipitations via chromium or zircon functions in the following manner. As is known, on account of their high thermal stability, manganese silicides already form during cooling of the melt before solidification of the basic structure of Cu-Zn-Al. Chromium or zircon or their compounds act as a nucleat-

ing agent for the silicide formation. Depending on the number of existing nucleating agents, i.e. dependent on the chromium or zircon content, a corresponding number of silicide precipitations are then formed which can only attain a specific average grain size through the limited manganese and silicon content in the alloy.

In particular, a fine eutectic precipitation of silicides is surprisingly also suppressed through the addition of chromium or zircon which in the state of the art makes up a large portion of the silicide quantity present without, however, making a correspondingly large contribution to the wearing quality.

Further possible additions to the alloy according to the invention are lead and nickel. The optional component lead may be added up to a content of approximately 2% and improves, in particular, the behaviour of the material during machining.

The optional component nickel may likewise be added up to a content of approximately 2% and preferably acts as a diffusion brake. Nickel is therefore only added when longer lasting heat treatments are planned for the material in which the structure should not change in an undesired manner if possible through diffusion.

The alloy is relatively tolerant with respect to its structural formation compared with the usual impurities resulting during the manufacture of brass. Therefore, the usual impurities are permissible in portions up to 1%. This does not pertain, however, to iron impurities. The iron portions in these impurities are preferably permissible only up to a maximum of 0.7%. Iron portions above this limit, particularly above 1%, make the melting in more difficult and influence the homogeneity of the manganese silicide precipitations.

As a result, the technical properties of the material deteriorate.

The manufacturing method for a material or semi-finished product having the alloy composition described above is relatively straight forward since the silicides decisive for the high wear resistance already are formed by primary precipitation.

10 In the manufacturing method according to the invention, the alloy melted in the usual manner is cast or preferably continuously cast at temperatures above approximately 1000°C and cooled at any rate of cooling to temperatures below 400°C. This cooled material or the semi-finished product, already partially formed through extrusion, exhibits a basic structure which, dependent on the portions of copper, zinc and aluminium and on the rate of cooling, consists of a pure β -mixed crystal structure, and with increasing copper equivalent (theoretical copper content) and falling rate of cooling consists of a $\beta+\alpha$ - mixed crystal structure, whereby the β -portion as a rule predominates.

20 The primary precipitations consisting for the most part of manganese silicide are deposited in this β or $\beta+\alpha$ -basic structure, preferably within the grains. These manganese silicides are distributed extremely homogeneously and are of a relatively uniform size on account of the chromium/zircon nucleation mechanism already described above. In this material the manganese silicides are present in the usual needle shape, whereby the diameter of the needles is preferably in the order of magnitude of up to approximately 5 μm and the length is up to approximately 30 μm .

The cast and, preferably, cooled material can be subjected to further hot forming steps in a temperature range between 550 and 800°C, preferably 620 and 720°C. Extrusion can be preferably employed as the first hot forming step and thereafter optionally, for example, drop forging.

It is furthermore possible, in connection with the individual forming steps, to carry out the heat treatment steps in a temperature range between 200 and 500°C. These heat treatment steps serve to relieve stress or to age harden the structure or to adjust specific structural ratios such as, for example, increasing the α -portion in the $\beta + \alpha$ -mixed crystal structure. The heating durations thereby lie in the range between a few seconds (for example, inductive heating prior to drop forging) and approximately 24 hours (for example, stress-relief annealing at lower temperatures).

10 Both the hot forming steps and the heat treatment steps for the most part only cause changes in the Cu-Zn-Al basic structure. By comparison, the manganese silicides present as primary precipitations are not affected.

On account of the silicide precipitations described, such brass materials or alloys can be used in an advantageous manner for semi-finished goods and intermediate products which must have a high resistance to wear in addition to good workability. Synchronizing disks for motor vehicle transmissions are preferably produced from this material.

Examples

20 Table I (below) gives the compositions of various alloys, the structure and wearing properties of which are considered in detail in the following.

The composition of alloys 1 and 2 or 3 and 4 are each identical except for the chromium content, whereby alloys 1 and 3 do not contain any chromium while alloys 2 and 4 each have a chromium portion of 0.05%.

The composition of alloys 5 to 7 is essentially identical (only the manganese content varies somewhat) except for the chromium content which in alloy 5 is equal to 0.10%, in alloy 6 is equal to 0.20% and in alloy 7

Table 1: compositions in % by weight

Alloy number	1	2	3	4	5	6	7	CuZn40Al 2
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Alloy constituent								
Cu	59,4	59,4	60,6	60,6	68,5	68,5	68,5	58,5
Zn	26,6	26,6	27,5	27,5	14,3	14,3	14,3	35,9
Mn	8,0	8,0	6,4	6,4	7,65	7,50	7,30	2,0
Al	2,5	2,5	2,5	2,5	6,0	6,0	6,0	1,6
Si	2,25	2,25	1,75	1,75	2,5	2,5	2,5	0,8
Cr	--	0,05	--	0,05	0,10	0,20	0,40	--
Pb	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,4
Impurities	only Fe analyzed, remainder consisting primarily of Ni and Sn							
Fe	0,5	0,5	0,5	0,5	0,3	0,3	0,3	0,5

is equal to 0.40%.

The alloy CuZn40Al 2 represents a standard synchronizing disk alloy for reference in the wearing comparison to be described later.

All of the alloys named in Table I were melted in a crucible furnace and at initial temperatures above 1000°C were poured in the continuous casting with a diameter of 220 mm. After cooling at an average rate of cooling, structural samples were taken which were prepared in the usual manner. Figures 1 to 7 (the number of the Figure is identical to the alloy number) show typical micrographs of this material at 200-fold magnification.

10 The structures illustrated in Figures 1 and 3 have extremely inhomogeneous manganese silicide precipitations (dark areas in the photo). In particular, the eutectic silicide precipitations already considered in connection with the state of the art are also recognizable (Figure 1: lower half of photo, centre; Figure 3: bottom left). The positive effect of the chromium additions of 0.05% on the homogeneity of the manganese silicide precipitations is easily recognizable in the structure according to Figures 2 and 4. The silicides are distributed substantially more evenly and have very similar dimensions (in the sectional view only a small portion of the randomly oriented, needle-shaped manganese silicide precipitations lie exactly in the cutting plane
20 so that only their cross-sections are visible). The further, partly recognizable fine lines in the light background in Figures 1 to 4 represent the grain boundaries of the basic structure. In particular, no eutectic silicide precipitations are recognizable.

Figures 5 to 7 show the effects of too high an addition of chromium (dark areas) on the manganese silicide precipitations (Figures 6 and 7) in comparison with the structure of the material according to the invention

(Figure 5).

In Figure 5 it is already recognizable that the silicide needles are smaller than in the structure according to Figure 4. This is a result of the twice as high chromium portion (Figure 4: 0.05%; Figure 5: 0.10%) with an only slightly increased silicon content (Figure 4: 2.25%; Figure 5: 2.5%).

Figure 6 shows another structure resulting from a doubled chromium content of 0.20%, whereby the other constituents are approximately identical to the alloy composition used for Figure 5. In this case the manganese silicide precipitations are already extremely fine and in such material result in a clearly deteriorated wearing quality. In addition, an unevenness in the distribution of the silicides is apparent in this structure (Figure 6, bottom right).

This unevenness is even clearer in the structure according to Figure 7, whereby with an otherwise almost identical composition the chromium content was again doubled (0.40%) in comparison to Figure 6. In addition to the too-fine manganese silicide precipitations, coarse silicide agglomerations which result in the unsuitableness of such material for the intended use are clearly recognizable in the structure according to Figure 6.

Synchronizing disks were manufactured according to the following preferred method from the material of alloy number 2 and from the material CuZn40Al 2 which serves as a standard reference. The continuously cast materials were extruded at 650°C into pipes having a diameter of approximately 85 x 70 mm. The pipes were subsequently cooled and cut up. The pipe pieces were heated inductively to 650°C and formed into synchronizing disks through drop forging. Thereafter, the synchronizing disks were stored at 250°C for 10 hours to harden. Wear samples were then taken from this intermediate

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product and a wear measurement was carried out according to the Reichert system which will be explained later. The results are given in Table II.

Table II: Wear Resistance

	Alloy No. 2	CuZn40 Al 2
Wear Resistance in km/g	1600 - 3100	150 - 200
Hardness HB 2.5/62.5	180	170
Share in the α -phase in % by volume	25	25

Apart from the resistance to wear which is given in kilometer per gram of material loss, Table II also gives the hardness of the test pieces and their structural share in the α -phase.

As can be seen from this, the hardness values of the two test pieces are almost the same; even the share in the α -phase is even exactly the same. These two dimensions are determined for the most part by the basic structure which is evidently very similar with respect to its technical properties.

The resistance to wear of the test pieces, which can basically be attributed to the silicide precipitations, is very different by comparison. All told, the wear in the test piece from alloy No. 2 is less by more than an order of magnitude than in the test piece made from the reference material.

To determine the resistance to wear values, a frictional wear balance of the Reichert system adapted for the present specific purpose was used. The test piece consisted of a round pin 2.7 mm in diameter, whose bearing surface was faced and which was taken from the synchronizing disk in such a way that its bearing surface originated from the area of the friction thread. A ground needle bearing ring made of 100 Cr 6 with an outer diameter of 35 mm,

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a hardness of 58 - 65 HRC and a bearing surface roughness of approximately $2\text{ }\mu\text{m}$ was used as the counter-body. The lubricant consisted of 75% by volume transmission oil SQ M2C - 9008 A and 25% by volume Shell Fususoil* 10 with an immersion depth of the needle bearing ring of 10 mm.

Test parameters used:

Load of the test piece 300 N corresponds to 52N/mm^2 ;

Rotational speed of the disk of 100 rpm corresponds to a rate of slide of approximately 1.8 m/sec.;

Lubricant temperature approximately 100°C ;

Running duration 2500 m.

10

The weight loss of the test piece is considered as the amount of wear, whereby the burr forming on the test piece is removed prior to determining the weight loss. The resistance to wear given in Table II is the ratio from the distance in kilometers and the weight loss in grams.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE
PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A brass alloy comprising (in % by weight):

10	to 35%	zinc
4	to 12%	manganese
2	to 7%	aluminium
1.1	to 4%	silicon
0.01	to 0.15%	chromium and/or zircon

provided that a majority of silicon is bound in the form of manganese silicide,

0	to 2%	lead
0	to 2%	nickel
0	to 1%	usual impurities,

whereby the portion of iron impurities does not exceed 0.7%, and the remainder
of the alloy is copper.

2. A brass alloy according to claim 1, wherein the silicon portion is
between 1.5 and 3%.

3. A brass alloy according to claim 1, wherein the chromium and/or
zircon portion is between 0.05 and 0.1%.

4. A brass alloy according to one of the claims 1 to 3, wherein the
manganese portion is at least 6%.

5. A brass alloy according to one of the claims 1 to 3, wherein the
manganese silicide content is higher than 5%.

6. A method for manufacturing a brass alloy defined in claim 1 or a
semi-finished product made from said brass alloy which comprises casting the

alloy, melted in the usual manner, at a temperature above 1000°C, cooling, at any rate of cooling, to temperatures below 400°C to obtain, in the cooled material, a β or $\beta+\alpha$ mixed crystal structure in which primary precipitations from essentially manganese silicides are deposited.

7. A method according to claim 6, wherein the cast material is hot formed, at a temperature of 550 to 800°C.

8. A method according to claim 7, wherein after the first hot forming a further hot forming step is carried out, in a temperature range of 550 to 800°C.

9. A method according to claim 7 or 8, wherein subsequent to the forming steps, a heat treatment to relieve stress or age-harden the structure or to adjust specific structural ratios is carried out in the temperature range between 200 and 500°C with a duration up to approximately 24 hours.

10. A method according to claim 6 wherein said casting is continuous casting.

11. A method according to claim 6 wherein said primary precipitations are deposited within the grains.

12. A method according to claim 7 wherein the cast material is extended at a temperature of 620 to 720°C.

13. A method according to claim 8 wherein said further hot forming step comprises drop forging at a temperature of 620 to 720°C.

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FIG. 1



FIG. 2

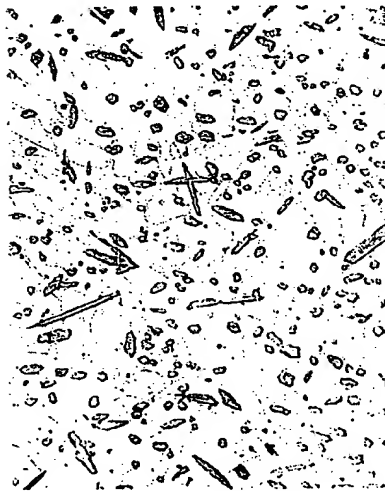
2-1



FIG. 3



FIG. 4



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FIG. 5



FIG. 6



FIG. 7



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